

Potential-Induced Aggregation of Anionic Porphyrins at Liquid|Liquid Interfaces

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Supporting Information

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at Liquid|Liquid Interfaces**

Sho Yamamoto,[†] Hirohisa Nagatani^{*,‡} and Hisanori Imura[‡]

[†] Division of Material Chemistry, Graduate School of Natural Science and Technology,
Kanazawa University, Kakuma, Kanazawa 920-1192, Japan

[‡] Faculty of Chemistry, Institute of Science and Engineering, Kanazawa University, Kakuma,
Kanazawa 920-1192, Japan

*To whom correspondence should be addressed: H. Nagatani

E-mail: nagatani@se.kanazawa-u.ac.jp

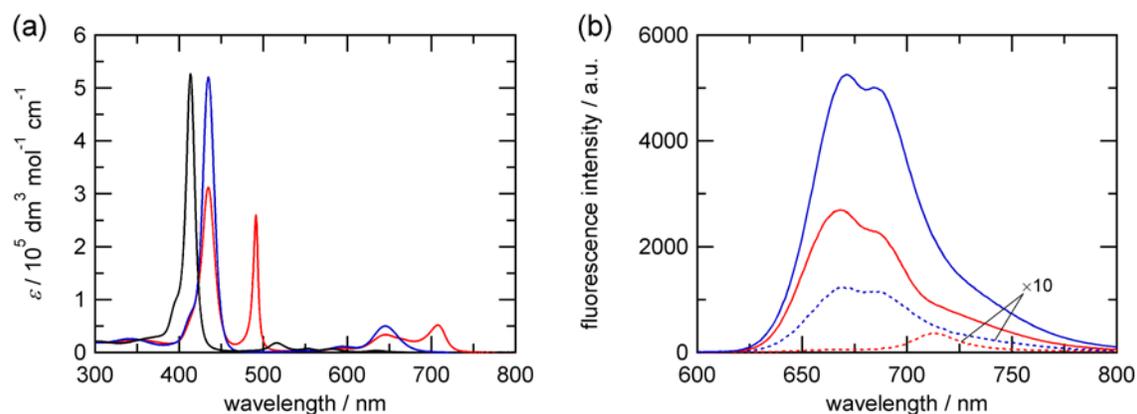


Figure S1. (a) UV-vis absorption and (b) fluorescence spectra measured for TPPS species in aqueous solution. The black, blue and red lines refer to pH 7.2, 2.3 and 1.3, respectively. The excitation wavelengths for the fluorescence measurement were 404 nm (solid line) and 488 nm (dotted line), respectively. The concentration of TPPS species and Li_2SO_4 were $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ and $1.0 \times 10^{-2} \text{ mol dm}^{-3}$. The pH conditions were adjusted by adding adequate amounts of H_2SO_4 or $\text{LiH}_2\text{PO}_4/\text{LiOH}$ buffer.

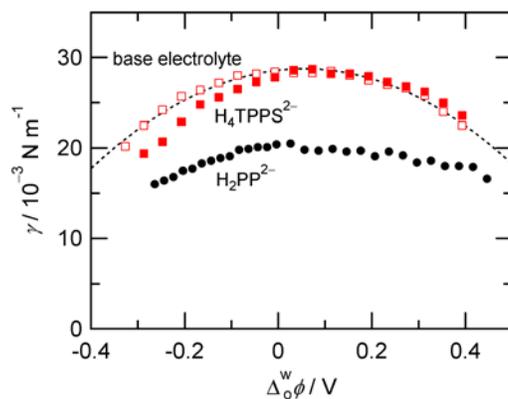


Figure S2. Electrocapillary curves measured by QELS for $\text{H}_4\text{TPPS}^{2-}$ system at pH 2.2 (**Cell I**, solid squares) and H_2PP^{2-} system at pH 7.2 (**Cell II**, solid circles). The concentration of $\text{H}_4\text{TPPS}^{2-}$ and H_2PP^{2-} were $2.0 \times 10^{-5} \text{ mol dm}^{-3}$ and $1.0 \times 10^{-4} \text{ mol dm}^{-3}$, respectively. In the base electrolyte system, $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ Li_2SO_4 was used as supporting electrolyte for the aqueous phase.

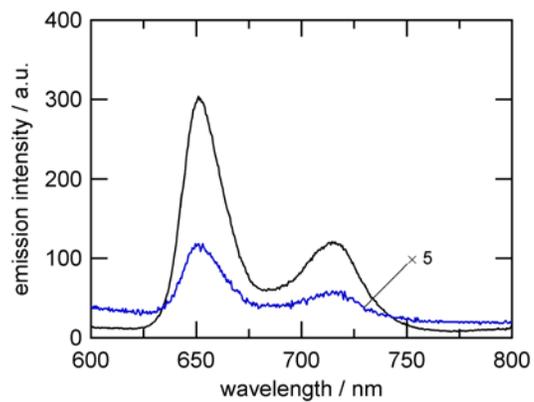


Figure S3. Fluorescence spectra measured for TPPS species in DCE after the electrochemical measurements with **Cell I**. The excitation light sources for the fluorescence measurement were cw laser diodes of 25 mW at 404 nm (black line) and 488 nm (blue line), respectively.

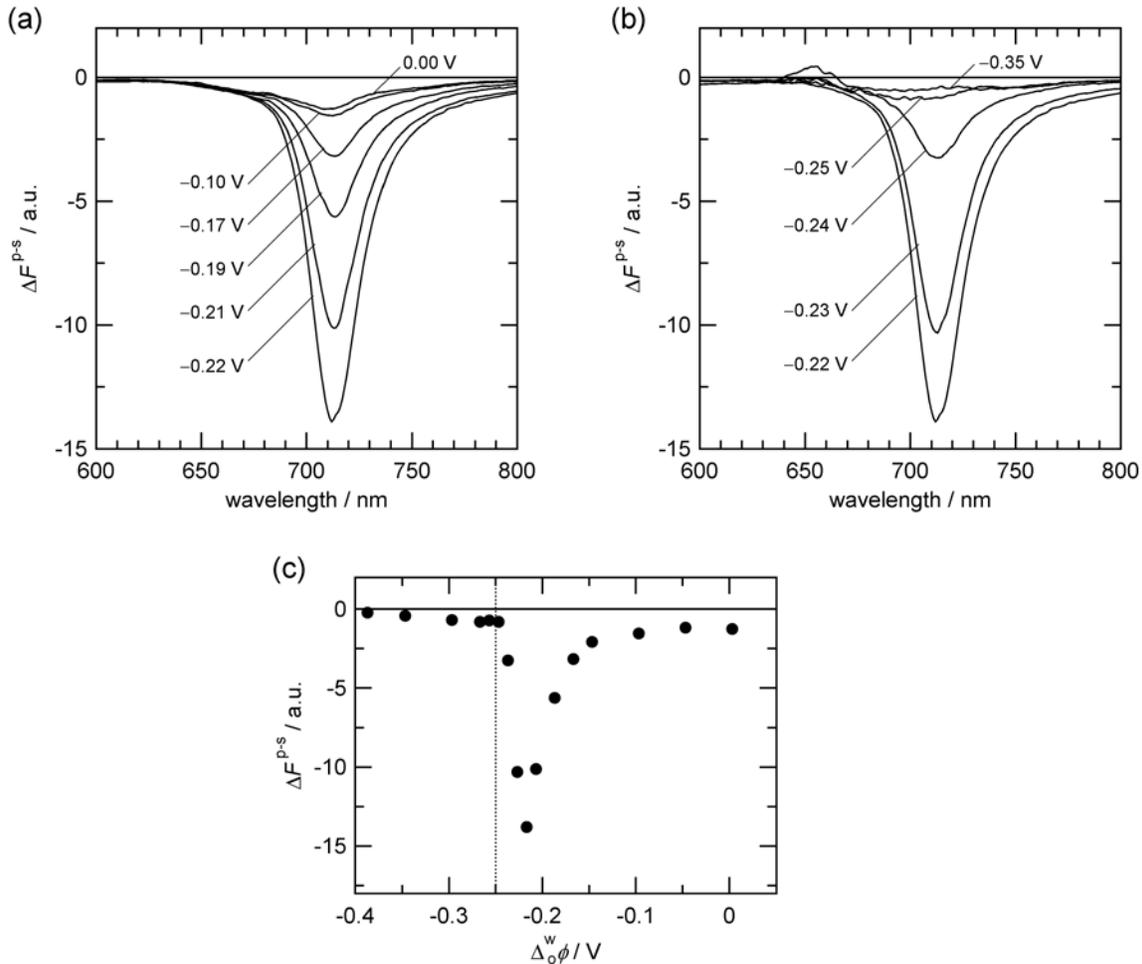


Figure S4. Typical spectral changes of PM-TIRF spectra for the $\text{H}_4\text{TPPS}^{2-}$ aggregates measured at the polarized water|DCE interface. The potentiostatic conditions were varied from (a) 0.00 V to -0.22 V and (b) -0.22 V to -0.35 V, respectively. The aqueous phase was adjusted at pH 2.2. The excitation wavelength was 488 nm. (c) ΔF^{P-s} at 713 nm vs. $\Delta_0^w \phi$ plot. The vertical dotted line depicts the ion transfer potential at pH 2.2.

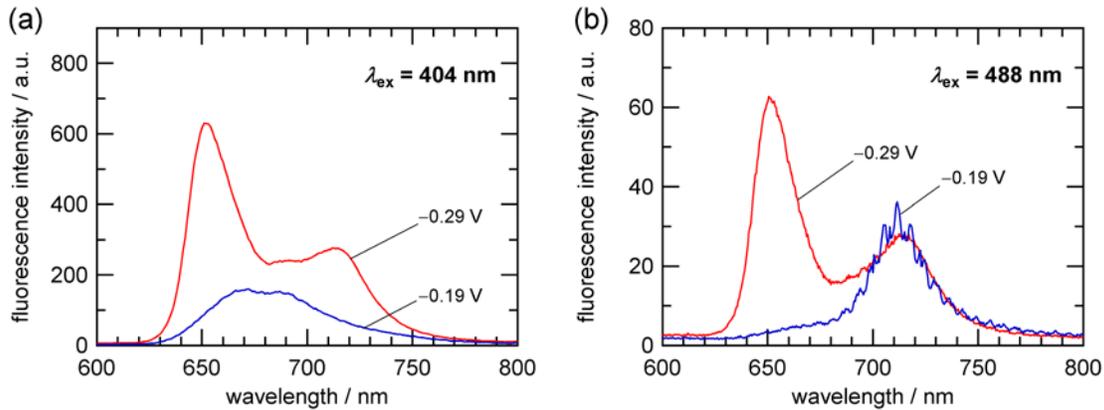


Figure S5. Conventional TIR fluorescence spectra measured at given potentials (**Cell I**). The excitation wavelengths were (a) 404 nm and (b) 488 nm, respectively.

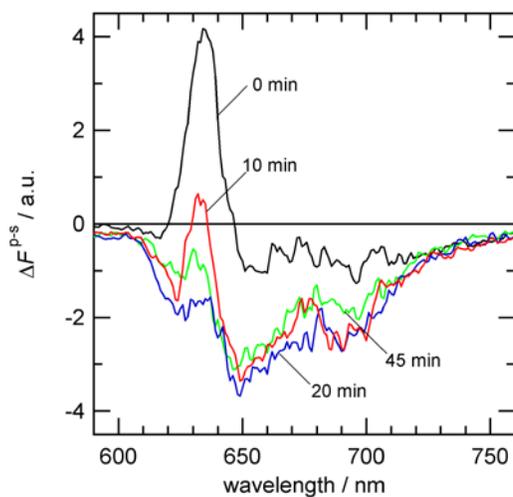


Figure S6. Time-dependence of PM-TIRF spectra for H_2PP^{2-} at -0.16 V. The concentration of H_2PP^{2-} was 1.0×10^{-4} mol dm^{-3} . The pH value of the aqueous phase was pH 7.2. See also **Table S1**.

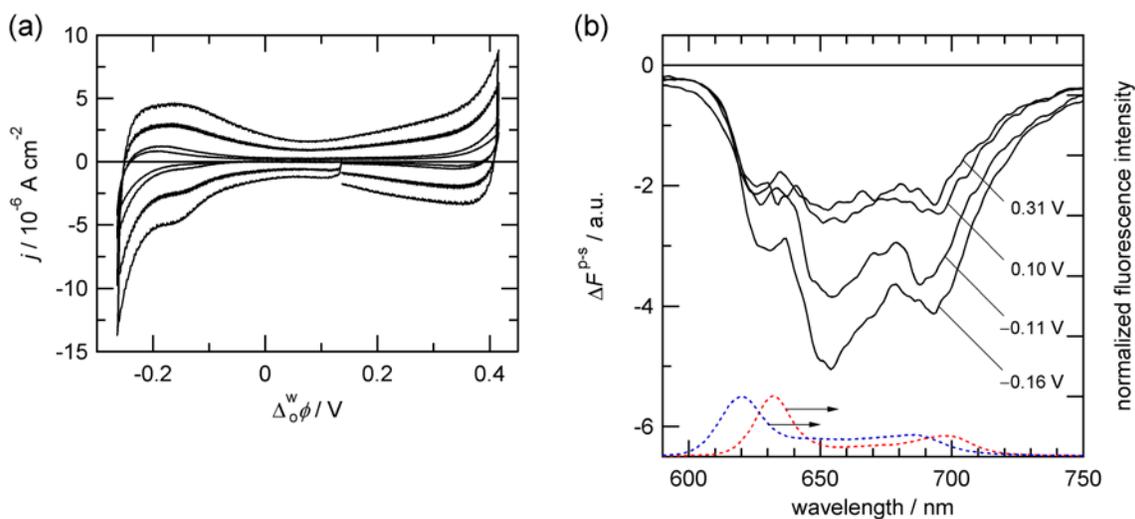


Figure S7. (a) CVs measured at 10, 20, 50, 100 mV s^{-1} and (b) PM-TIRF spectra for H_2PP^{2-} at the water|DCE interface. (b) The blue and red dotted lines refer to normalized fluorescence spectra measured in the aqueous and organic solutions, respectively. The concentration of H_2PP^{2-} was $2.0 \times 10^{-5} \text{ mol dm}^{-3}$. The pH value of the aqueous phase was pH 7.1.

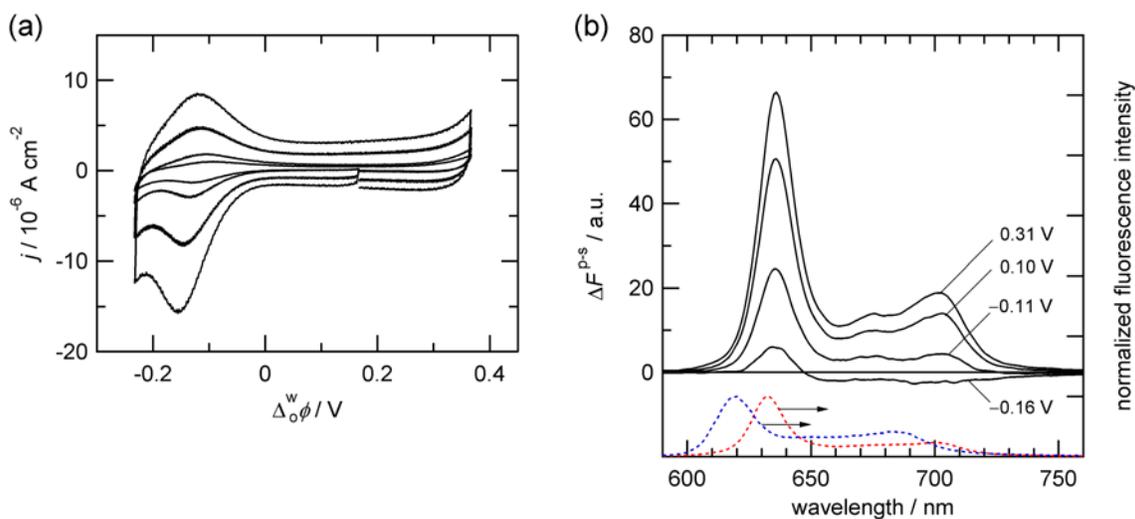


Figure S8. (a) CVs measured at 10, 20, 50, 100 mV s^{-1} and (b) PM-TIRF spectra for H_2PP^{2-} at the water|DCE interface. (b) The blue and red dotted lines refer to normalized fluorescence spectra measured in the aqueous and organic solutions, respectively. The concentration of H_2PP^{2-} was $5.0 \times 10^{-4} \text{ mol dm}^{-3}$. The pH value of the aqueous phase was pH 7.3.

Table S1. The maximum wavelengths of PM-TIRF spectra.

PP system		
$\Delta_o\phi / \text{V}$	time / min	$\lambda_{\text{em, max}}^{404} / \text{nm}$
-0.16 V	0	634(+)
	10	633(+)
	20	650(-), 694(-)
	45	647(-), 694(-)

See also **Figure S6**. The parenthetic signs (+) and (-) denote the positive and negative PM-TIRF peaks, respectively.